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Phase Behavior of Deuterated Polystyrene-*block*-poly(*n*-pentyl methacrylate) Copolymers

Du Yeol Ryu,[†] Unyong Jeong,[†] Dong Hyun Lee,[†] Jehan Kim,[‡] Hwa Shik Youn,[‡] and Jin Kon Kim*,[†]

Department of Chemical Engineering and Polymer Research Institute,
Electronic and Computer Engineering Divisions, Pohang Accelerator Laboratory,
Pohang University of Science and Technology, Kyungbuk 790-784, Korea

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ABSTRACT: The phase behavior of deuterated polystyrene-*block*-poly(*n*-pentyl methacrylate) copolymers (dPS−PnPMA) was investigated by using small-angle X-ray (SAXS) and neutron (SANS) scatterings and rheology. This block copolymer exhibited a closed-loop type of phase behavior as did hydrogenated PS−PnPMA copolymers. The closed loop consists of two transitions: lower disorder-to-order transition (LDOT) and upper order-to-disorder transition (UODT) occurring at a lower and higher temperature, respectively. The segmental interaction parameter (χ) between dPS and PnPMA blocks at various temperatures was obtained by fitting the incompressible random phase approximation theory to SANS results using a low molecular weight of dPS−PnPMA exhibiting a disordered homogeneous state over the entire temperature range. We found that at higher temperatures χ increased initially with increasing temperature (T), achieved a maximum, and then decreased. Such behavior is in keeping with polymer blends or block copolymers that would exhibit a closed-loop phase behavior. However, at temperatures below LDOT, χ did not decrease monotonically with decreasing T. Rather, with decreasing T, χ decreased initially, achieved a minimum, and then increased again. This strongly suggests that another transition of order-to-disorder transition (ODT) might be expected at lower temperatures.

I. Introduction

The phase behavior in polymer/polymer mixtures and block copolymers has been studied extensively,[1−6] both theoretically and experimentally. In general, upon heating, enthalpic repulsive interactions between constituent segments are weakened, resulting in a transition from a phase-separated to a phase-mixed state.[1−3] This phase transition has been referred to as the upper critical solution transition (UCST) for polymer mixtures and the order-to-disorder transition (ODT) for block copolymers.

Some polymer mixtures[7−9] and block copolymers[10−14] undergo a transition from the phase-mixed to phase-separated state on heating. This is referred to as the lower critical solution transition (LCST) for polymer mixtures and the lower disorder-to-order transition (LDOT) for block copolymers. It is known that the difference in thermal expansion coefficients of two segments, the so-called free volume effect,[7,8] increases with increasing temperature; when this effect dominates over the reduction in the enthalpic repulsive energy, LCST (or LDOT) occurs. Thus, a positive volume change on demixing is accompanied. Equation-of-state theories[7,8] and other theoretical approaches[15−22] related to the compressible random phase approximation (RPA) have been used to describe LCST and LDOT. Ruzette et al.[23,24] developed a compressible regular solution theory and predicted phase behaviors of polystyrene-*block*-poly(*n*-alkyl methacrylate) copolymers are in good agreement with the experimentally measured ones.

Using the RPA model combined with the compressible lattice-cluster theory, Dudowicz and Freed[16] predicted the coexistence of both LDOT at a low temperature and upper order-to-disorder transition (UODT) at a high temperature (thus a closed-loop phase behavior) in the polystyrene-*block*-poly(vinyl methyl ether) (PS−PVME) copolymer for the first time. But, Hashimoto and co-workers[20] could not experimentally detect a closed loop phase behavior of PS−PVME; rather, only the possibility of LDOT. Furthermore, only LDOT, not a closed loop, was predicted for PS−PVME when another compressible RPA developed by Hino and Prausnitz[21] and Cho[22] is employed. Gromov et al.[19] predicted a closed-loop phase behavior for the polymer/solvent system with no specific interaction in the aid of expanded Gibbs ensemble simulations.

The coexistence of both UCST (or ODT) and LCST (or LDOT) in a polymer blend system was predicted theoretically a long time ago.[3] However, Russell and co-workers[10] first found in 1994 both ODT and LDOT using PS-*block*-poly(*n*-butyl methacrylate) copolymer, although mixtures of polymer/solvent[25] and polymer/random copolymer[26,27] exhibited this behavior. Very recently, Kim and co-workers[28] found that polystyrene-*block*-poly(*n*-pentyl methacrylate) copolymers (PS−PnPMA) exhibit closed-loop phase behavior composed of both LDOT and UODT occurring at a lower and a higher temperature, respectively. LDOT and UODT in the closed-loop phase transition are shifted toward higher and lower temperature, respectively, with decreasing molecular weight of block copolymer. This suggests that the size of the closed-loop phase boundary decreases with decreasing of the degree of polymerization (or total number of segments), N.

Closed-loop phase behavior was first reported a century ago for the water/nicotine mixture.[29] Mixtures of poly(ethylene oxide)/water and poly(vinyl alcohol-*co*-

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[†] Department of Chemical Engineering and Polymer Research Institute.

[‡] Pohang Accelerator Laboratory.

* To whom correspondence should be addressed: e-mail jkkim@postech.ac.kr.

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vinyl acetate)/water also exhibited the same phase behavior.[30] These systems have strong specific directional interactions such as hydrogen bonding at lower temperatures. Since specific directional interactions decrease with increasing temperature, LCST is expected. But, with further increasing temperature, entropic contribution prevails over any unfavorable interaction; thus, upper UCST can be observed. This upper UCST (or upper UODT) had not been observed for polymer blend or block copolymer with a weak interaction before Kim and co-workers[28] found it very recently. This might be simply because most polymer systems degrade thermally before the mixing entropy dominates.

According to Ruzette,[31] a closed loop found in PS−PnPMA is attributed to a delicate balance between enthalpic and entropic contributions to free energy of mixing. There might exist a weak interaction between PS and PnPMA segments even if strong directional interactions such as hydrogen bonding are absent. A weak interaction becomes negligible compared with entropic contribution to free energy of mixing for a mixture with a low molecular weight component. However, for polymer mixtures (or block copolymer), the entropic contribution is reduced to $1/N$ compared with a mixture having at least one low molecular weight component. Thus, for weakly interacting polymer systems, the entropic contribution to free energy arising free volume effect can compete with the enthalpic contribution, giving rise to a LCST (or LDOT) at intermediate temperatures. At high temperatures, translational entropic contributions prevail over any unfavorable interaction, and thus upper UCST (UODT) was observed.

On the other hand, we showed that binary polymer blends of dPS/PnPMA and PS/PnPMA did not exhibit a closed loop; rather, those have another phase diagram with the combination of both UCST and LCST which occurred at a lower and a higher temperature, respectively.[32] With increasing molecular weight, these two phase boundaries merged into an hourglass type. It is known from thermodynamics that closed-loop phase behavior is expected for a blend (or a block copolymer) when the segmental interaction parameter (χ) of constituent components becomes a maximum with increasing T.[33] But, another phase behavior having the combination of both UCST and LCST (and hourglass) would be seen for a blend (or block copolymer) when χ becomes a minimum with increasing T.[33]

According to the mean-field approximation, the phase behavior of a polymer blend should be correlated to that of the corresponding block copolymer provided that one takes into account the differences in the molecular weights to satisfy the critical conditions.[34] To reconcile two different phase behaviors between PS−PnPMA block copolymer and PS/PnPMA blend, the temperature dependence on χ between PS and PnPMA should be investigated. In this paper, we report on the phase behavior of symmetric deuterated PS-*block*-PnPMA (dPS−PnPMA) by using small-angle X-ray and neutron scatterings (SAXS and SANS, respectively), rheology, and transmission electron microscopy (TEM). Then, using Leibler's RPA theory,[6] we determined χ over the entire temperature range by using a homogeneous dPS−PnPMA. We observed abnormal temperature dependence of χ between dPS and PnPMA, which might be a clue to interpreting the difference of phase behavior between the dPS−PnPMA and dPS/PnPMA blend. Here, we report on our highlights.

Table 1. Molecular Characteristics of dPS−PnPMAs Employed in This Study

sample code	M_n[a]	M_w/M_n[a]	N[c]
dPS−PnPMA−L	46 000	1.02	347
dPS−PnPMA−BL[b]	49 300		372
dPS−PnPMA−BM[b]	49 700		375
dPS−PnPMA−BH[b]	50 000		377
dPS−PnPMA−H	53 300	1.03	402

[a] Measured by multiangle laser light scattering combined with SEC. [b] dPS−PnPMA−BL, dPS−PnPMA−BM, and dPS−PnPMA−BH were prepared by blending of dPS−PnPMA−H and dPS−PnPMA−L. The weight fractions of dPS−PnPMA−H and dPS−PnPMA−L are 0.45/0.55 in dPS−PnPMA−BL, 0.50/0.50 in dPS−PnPMA−BM, and 0.55/0.40 in dPS−PnPMA−BH. [c] Total numbers of segments (N) were calculated from eqs 1 and 2b. Using $v_{sp,dPS} = 0.87$ cm^3/g and $v_{sp,PnPMA} = 0.97$ cm^3/g measured at room temperature, v_{ref} was calculated to be 122.66 cm^3/mol by eq 2b.

II. Experimental Section

Two symmetric deuterated polystyrene-*block*-poly(*n*-pentyl methacrylate)s, denoted as dPS−PnPMA, having number-average molecular weights (M_n) of 46 000 (dPS−PnPMA−L) and 53 300 (dPS−PnPMA−H), are synthesized by the sequential, anionic polymerization of deuterated styrene and *n*-pentyl methacrylate in tetrahydrofuran (THF) at −78 °C in the presence of LiCl under purified Ar using a *sec*-BuLi initiator. LiCl (high purity, Aldrich) was dried overnight at 150 °C and then dissolved in dried THF. The THF was purified first by refluxing over CaH_2 and then by stirring over fresh sodium−benzophenone complex until it showed a deep purple color, indicating an oxygen- and moisture-free solvent. Before the polymerization, deuterated styrene (99.5%, CDN isotopes) and pentyl methacrylate (high purity, Scientific Polymer Products Inc.) were first vacuum-distilled from CaH_2 after degassing to remove moisture and then distilled over of dried dibutylmagnesium and trioctylaluminum, respectively, until a persistent characteristic color was observed: yellow for dPS and yellowish-green for PnPMA. It took 1 h to synthesize deuterated styrene for full conversion. A small quantity of first polymerized solution was transferred into a tube and then terminated with purified 2-propanol to determine the molecular weight of dPS block. After pentyl methacrylate monomer was introduced very slowly into the reactor and then stirred for 5 h, the polymer solution terminated with purified 2-propanol was precipitated in methanol/water (80/20 w/w) mixture.

The weight-average molecular weights (M_w) and M_n were measured by multiangle laser light scattering with size exclusion chromatography (SEC). The polydispersity index (M_w/M_n) of dPS−PnPMAs was less than <1.03. The volume fraction of the dPS block was 0.5 as determined by nuclear magnetic resonance and mass densities measured at room temperature of the two components (1.15 and 1.03 g/cm^3 for dPS and PnPMA). Since a small difference in M_n of dPS−PnPMA dramatically changes phase behavior, we prepared three mixtures of dPS−PnPMA−L and dPS−PnPMA−H having M_n's of 49 300 (dPS−PnPMA−BL), 49 700 (dPS−PnPMA−BM), and 50 000 (dPS−PnPMA−BH). Thus, these three block copolymers have $M_w/M_n < 1.04$. The molecular characteristics of dPS−PnPMAs employed in this study are given in Table 1.

Samples for small-angle X-ray and neutron scatterings (SAXS and SANS, respectively) were prepared by compression-molding at 115 °C, followed by annealing at 120 °C under vacuum for 24 h. It is noted that all block copolymers except dPS−PnPMA−H become disordered at 120 °C. SANS experiments were performed at the Hanaro Reactor (Korea) with a $\lambda = 0.431$ nm and $\Delta\lambda/\lambda = 0.12$ at a sample-to-detector distance of 3 m. Scattering intensities were collected on a 2-D area detector and then circularly averaged. The sample thickness was 1 mm, and the exposure time was 1 h. SANS profiles at temperatures higher than 120 °C were obtained at every 10 °C during heating. Before SANS profiles were measured, the samples were equilibrated for 1 h at each temperature. However, to measure SANS profiles at lower temperatures

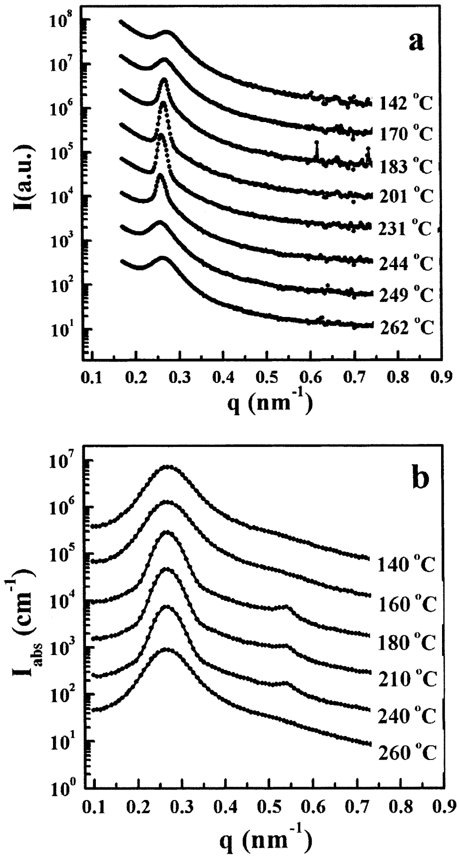

Figure 1. (a) Small-angle X-ray scattering (SAXS) profiles ($I(q)$ vs q) and (b) small-angle neutron scattering (SANS) profiles at various temperatures for dPS−PnPMA−BH. To avoid overlap, all profiles are vertically shifted by a factor of 6.

than 120 °C, the samples were first very slowly cooled at a rate of 10 °C/day to 70 °C from 120 °C. Then SANS profiles were obtained during heating at every 10 °C with a soaking time of 1 h at each temperature. It should be noted that SANS profiles measured as low as 80 °C could correspond to equilibrium morphology even though the T_g of dPS block was ∼100 °C. This is because the T_g of dPS−PnPMA in the homogeneous state was ∼57 °C measured by a dilatometer (DIL402, Netzsch Co.).[35]

Synchrotron SAXS measurements were performed on a Beamline 4C1 at the Pohang Light Source (Korea) where W/B4C double multilayer monochromator delivered monochromatic X-rays with a wavelength (λ) of 0.1608 nm and a resolution $\Delta\lambda/\lambda \cong 0.01$ onto the sample.[36] A flat Au mirror was used to reject the higher harmonics from the beam. A 2-D CCD camera (Princeton Instruments Inc., SCX-TE/CCD-1242) was used to collect the scattered X-rays. The sample thickness was 1.5 mm, and the exposure time was 5 min.

An Advanced Rheometric Expansion System (Rheometrics Co.) with 40 mm diameter parallel plates was used to determine the shear modulus of dPS−PnPMA from 115 to 265 °C at a heating rate of 0.5 °C/min. A strain amplitude of 0.05 and angular frequency of 0.1 rad/s, which lie in linear viscoelasticity, were used.

III. Results and Discussion

Figure 1a gives SAXS profiles ($I(q)$ vs q ($= 4\pi \sin \theta/\lambda$); here, q is the scattering vector and 2θ is the scattering angle) for dPS−PnPMA−BH taken from 140 to 265 °C at a heating rate of 0.5 °C/min. SANS profiles at various temperatures are shown in Figure 1b. According to Figure 1a, at temperatures lower than 170 °C, a broad maximum in the scattering is observed arising from the correlation hole scattering of a block copolymer in the disordered state.[6,36] With increasing temperature, the SAXS profile sharpens and becomes a very sharp peak at $q_{\max} = 0.26{-}0.27$ nm^{-1} depending on temperature. Here, $q_{\max}$ is a scattering vector corresponding to a maximum scattering intensity. Thus, this block copolymer has the LDOT.

Interestingly, with further increasing temperature, the SAXS intensity begins to decrease. At temperatures higher than 249 °C, a diffuse and weak scattering maximum appears, which is again characteristic of a disordered block copolymer. This transition is referred to as upper order-to-disorder transition (UODT). From the existence of the LDOT at a low temperature as well as the UODT at a high temperature, dPS−PnPMA−BH exhibits a closed-loop phase behavior. Previously, we reported that hydrogenated PS−PnPMA exhibited the same phase behavior.[28]

Even though a synchrotron source of X-ray with a relatively longer exposure time (5 min) was used, we could not find higher-order peaks in SAXS profiles given in Figure 1a. This is due to very small X-ray contrast between dPS (or PS) and PnPMA blocks. A conventional rotating anode X-ray generator (18 kW, Rigaku Co., operated at 50 kV × 20 mA) did not give any discernible first-order peak of this block copolymer even though exposure time was as large as 30 min. Since the volume fraction of dPS block is 0.5, microdomains at temperatures corresponding to inside the closed loop (or $167 < T < 248$ °C) are expected to be lamellar (LAM). This was verified by TEM images (not shown here). We found that the Bragg spacing of LAM ($2\pi/q_{\max}$) of 24 nm was consistent with the TEM image. At temperatures between 180 and 240 °C, a higher-order peak ($2q_{\max}$) corresponding to LAM is clearly seen (Figure 1b). Although the first-order peak in SANS profiles is much broader than that in SAXS profiles in Figure 1a, the peak position in SANS and SAXS profiles is essentially the same.

Figure 2a gives plots of the inverse of the maximum scattered intensity ($1/I(q_{\max})$) and the full width at half-maximum (fwhm) vs the inverse temperature ($1/T$) for four different dPS−PnPMAs. In Figure 2b are given those plots of dPS−PnPMA-BH from SANS experiments. The highest molecular weight dPS−PnPMA-H exhibits very high scattering intensity and narrow fwhm, which is a typical ordered state (Figure 2a). A small decrease in M_n (∼6%) gives completely different behavior. For instance, for dPS−PnPMA−BH, a rapid decrease in $1/I(q_{\max})$ and fwhm is observed near 170 °C, corresponding to LDOT. Then is seen a more rapid increase in $1/I(q_{\max})$ and fwhm near 240 °C corresponding to UODT. The UODT occurs over a much narrower temperature interval (∼5 °C) than the LDOT (∼15 °C). The same behavior is seen in Figure 2b. Note that SANS experiments were done at every 10 °C during heating and annealed at each temperature for 1 h, whereas SAXS experiments were done at every 2.5 °C with heating rate of 0.5 °C/min. With decreasing molecular weight, the LDOT increases and the UODT decreases. dPS−PnPMA−L, whose molecular weight is the lowest among block copolymers employed in this study, has a very low intensity of SAXS profile over the entire temperature range, even though a broad but very small peak could be seen due to a correlation hole effect. Because of small values of signal-to-noise ratio of this block copolymer, $1/I(q_{\max})$ and fwhm are not ac-

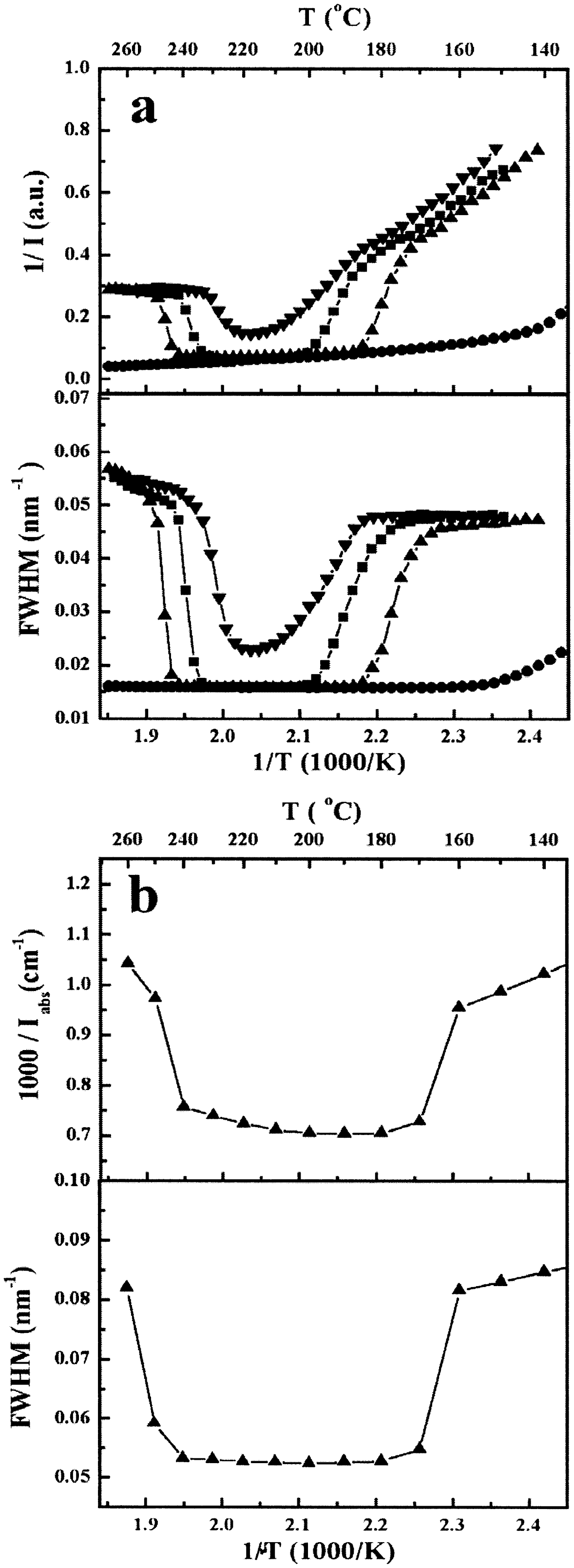

Figure 2. (a) Plots of $1/I(q_{\max})$ and fwhm obtained from SAXS results vs $1/T$ for various dPS−PnPMAs: dPS−PnPMA−BL (▼), dPS−PnPMA−BM (■), dPS−PnPMA−BH (▲), and dPS−PnPMA−H (●). (b) Plots of $1/I(q_{\max})$ and fwhm obtained from SANS results vs $1/T$ for dPS−PnPMA−BH.

curately obtained; thus, these data are not added in Figure 2a.

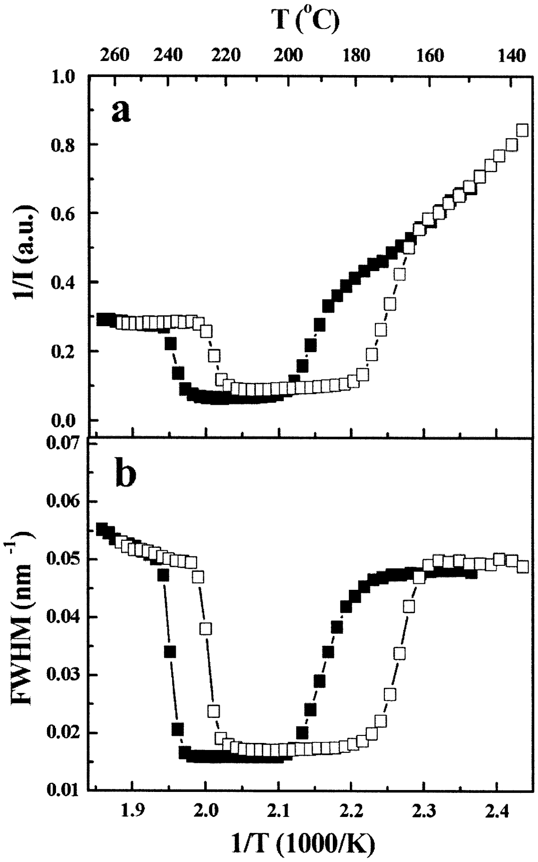

Figure 3. Plots of (a) $1/I(q_{\max})$ and (b) fwhm vs $1/T$ obtained SAXS profiles for dPS−PnPMA−BM during heating (closed symbols) and cooling (open symbols) at a rate of 0.5 °C/min.

To find whether LDOT and UODT are thermoreversible, we obtained SAXS profiles of dPS−PnPMA−BM during cooling from 270 °C at a rate of 0.5 °C/min. The plots of $1/I(q_{\max})$ and fwhm vs $1/T$ are shown in Figure 3, where those plots obtained during heating (closed symbols) at a rate of 0.5 °C/min are added. With decreasing temperature, dPS−PnPMA−BM first becomes ordered near 220 °C and then disordered near 170 °C. These two temperatures are ~10 and ~ 20 °C lower than those obtained during heating. Thus, even if a small rate of heating and cooling (0.5 °C/min) is used, a hysteresis exists. However, this hysteresis was not discernible (<1 °C) if we reduce heating and cooling rate less than 1 °C/h. This experiment was done with a static birefringence experiment instead of synchrotron SAXS experiment due to the limited beam time. It is also noted from Figure 3 that the SAXS intensity and fwhm obtained from heating and cooling cycles are essentially the same in the disordered (or homogeneous) state occurring at both low and high temperatures, which implies that thermal equilibrium was achieved in the homogeneous state.

The LDOT and UODT are easily determined from temporal change in G', which is given in Figure 4. For dPS−PnPMA−L, G' is seen to monotonically decrease with increasing temperature, typical for a homogeneous, disordered block polymer.[37−42] With increasing molecular weight of dPS−PnPMA, a sharp increase in G' was observed at a lower temperature corresponding to LDOT,[13] while a sharp decrease in G' was seen at a higher temperature corresponding to UODT. For dPS−PnPMA-H whose M_n is the largest in this study, high values of G' were maintained even at high temperatures, indicating that this block copolymer remains ordered up to ~270 °C, above which PnPMA block can degrade thermally. We found that the temperatures at

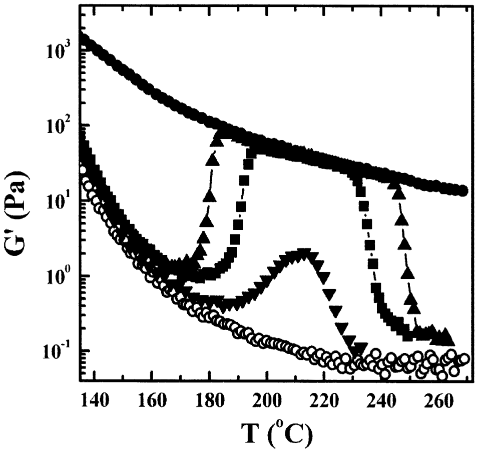

Figure 4. Temporal change in the shear modulus (G') for various dPS−PnPMAs: (○) dPS−PnPMA−L, (▼) dPS−PnPMA−BL, (■) dPS−PnPMA−BM, (▲) dPS−PnPMA−BH, and dPS−PnPMA−H (●).

which the transitions are observed rheologically are in good agreement with those obtained from SAXS experiments. The results that (i) dPS−PnPMA has both LDOT at a lower temperature and UODT at a higher temperature and (ii) these two transitions are very sensitive to molecular weight are essentially the same phenomena for hydrogenated PS−PnPMA (hPS−PnPMA) reported previously.[28]

The changes of LDOT and UODT with M_n of dPS−PnPMA are given as closed symbols in Figure 5a, where those of hPS−PnPMA (open symbols) are added for comparison. Both block copolymer systems give dramatic changes of both LDOT and UODT with M_n. However, the densities of dPS and PnPMA are 1.15 and 1.03 g/cm^3 at room temperature, respectively, while the density of hPS is 1.05 g/cm^3. Since the volume fraction of dPS (and hPS) block is 0.5 for both block copolymers, the total number of segments (N) is a more appropriate parameter than total molecular weight (M_n). Here, N is defined as

$$N = (V_{\mathrm{dPS}} + V_{\mathrm{PnPMA}})/v_{\mathrm{ref}} \qquad (1)$$

where V_{dPS} and V_{PnPMA} are molar volumes of dPS and PnPMA blocks. Between two expressions of v_{ref}, in this study eq 2b was employed.

$$v_{\mathrm{ref}} = v_{\mathrm{sp,PnPMA}}[\mathrm{M}]_{0,\mathrm{PnPMA}} \qquad (2a)$$

$$v_{\mathrm{ref}} = (v_{\mathrm{sp,dPS}}[\mathrm{M}]_{0,\mathrm{dPS}}v_{\mathrm{sp,PnPMA}}[\mathrm{M}]_{0,\mathrm{PnPMA}})^{1/2} \qquad (2b)$$

in which $v_{\mathrm{sp},i}$ and $[\mathrm{M}]_{0,i}$ (i = dPS, PnPMA) are the specific volume (cm^3/g) and monomer molecular weight of component i, respectively.

Figure 5b shows the dependence of LDOT and UODT on N for dPS−PnPMA and hPS−PnPMA block copolymers. With increasing N (or M_n), the LDOT decreases while the UODT increases, which gives a large ordered region. Outside of these two temperatures, the copolymer becomes disordered. At a given N, the LDOT of dPS−PnPMA is essentially the same as that of hPS−PnPMA, whereas the UODT of the former is ∼50 °C higher than that of the latter. Extrapolation of the data to a lower N suggests that the dPS−PnPMA and hPS−PnPMA will not become ordered for $N < 360$ and $N < 370$, respectively. These results indicate that the miscibility (or $1/\chi$) between dPS and PnPMA is slightly worse than that of hPS and PnPMA because of the effect of the deuterium substitution on χ,[43] although the difference is very small.

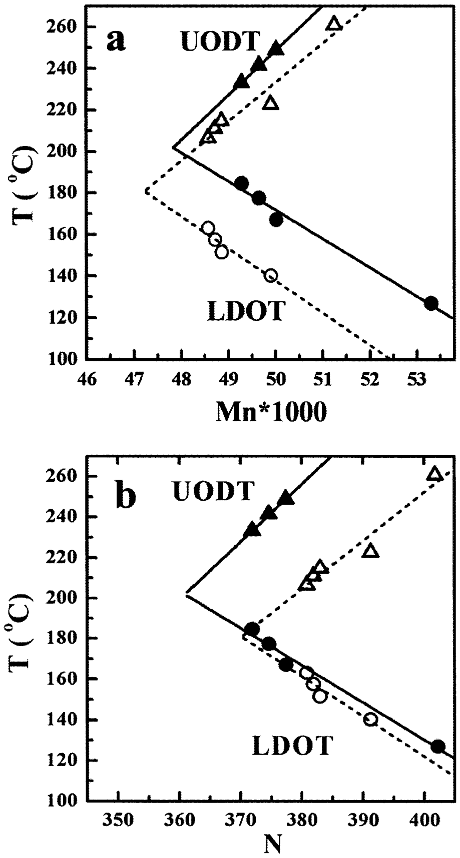

Figure 5. Dependence of LDOT (circles) and UODT (triangles) on (a) number-average molecular weight and (b) total number of segments for various dPS−PnPMAs (closed symbols) and PS−PnPMAs (open symbols). All lines were drawn on the basis of a least-squares method.

This strong dependence of the transition temperature on N (or M_n) allows us to see a closed-loop phase behavior. Namely, a subtle balance between the segmental enthalpic interaction and entropic contribution from equation-of-state effect can be easily altered by a small change in total number of segments (or M_n).[28,31] However, as stated in a previous communication,[32] the phase behavior of hPS−PnPMA is completely different from that of the hPS/PnPMA blend where the hourglass type, not closed-loop type, of phase behavior was observed. We further reported that χ between dPS and PnPMA in block copolymer increased initially with increasing T, achieved maximum values, and then decreased. On the other hand, χ between dPS and PnPMA in blend decreased initially with increasing T, achieved minimum values, and then increased.[32] Even though a different phase behavior between block copolymer and polymer blend was predicted by Dudowicz and Freed[16] for the PS−PVME copolymer and PS/PVME blend, we still could not come up with a reasonable explanation. Furthermore, in a previous paper, we only presented four data points of χ for dPS−PnPMA−L.[32] Thus, we carried out SANS experiments of dPS−PnPMA-L at a wide temperature range (80 °C < T < 270 °C). This block copolymer becomes disordered state at the entire temperature range; thus, the measured SANS profiles even at temperature lower than T_g of PS

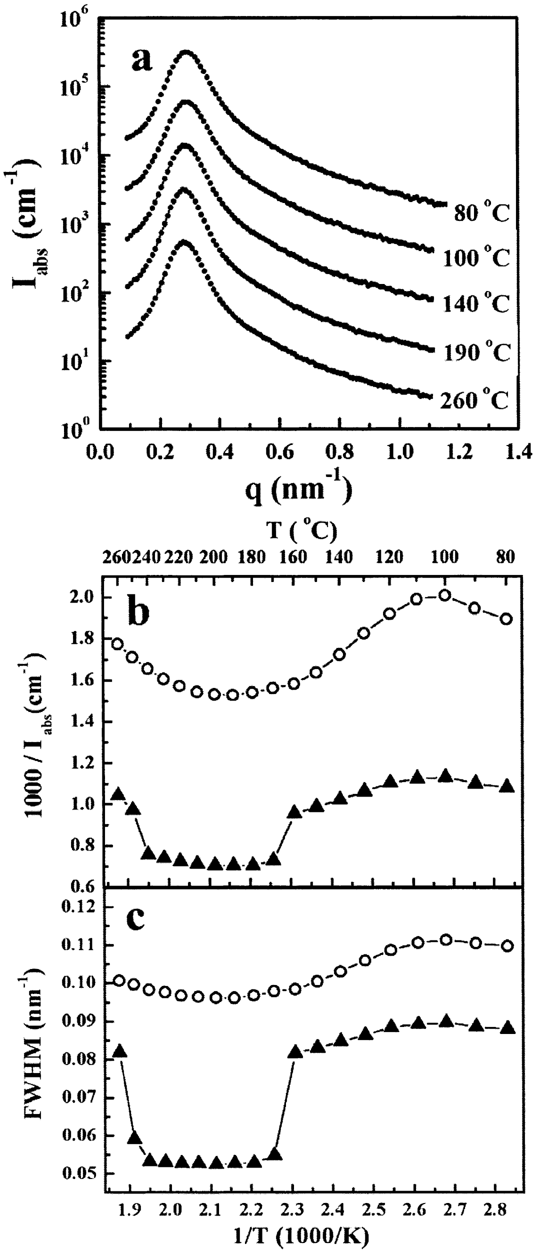

Figure 6. (a) SANS profiles at various temperatures for dPS−PnPMA−L. To ovoid overlap, SANS profiles are vertically shifted by a factor of 5. Plots of (b) $1/I(q_{\max})$ and (c) fwhm vs $1/T$ for dPS−PnPMA−L (○) and dPS−PnPMA−BH (▲).

block (~100 °C) represent an equilibrium morphology, since the T_g of dPS−PnPMA−BH in homogeneous state was ~57 °C.[35]

Figure 6a gives SANS profiles of dPS−PnPMA−L at various temperatures, which clearly shows that this block copolymer becomes disordered over the entire temperature range. The plots of $1/I(q_{\max})$ and fwhm vs $1/T$ are given in parts b and c of Figure 6, respectively. Also, added in Figure 6b,c are those plots for dPS−PnPMA−BH which show two transitions of LDOT and UODT. Parts b and c of Figure 6 show that $1/I(q_{\max})$ and fwhm of dPS−PnPMA−L become a minimum near 190 °C, even though this block copolymer becomes disordered at this temperature. Surprisingly, at lower temperatures (less than 140 °C), $1/I(q_{\max})$ and fwhm of dPS−PnPMA−L do not monotonically increase with decreasing temperature; rather, these two become a maximum near 100 °C, although the maximum of fwhm is not evident compared with that of $1/I(q_{\max})$. We also found that $1/I(q_{\max})$ and fwhm of dPS−PnPMA-BH have a maximum near 100 °C, at which the temperature corresponds to the disordered state.

These results suggest that at lower temperature regions the miscibility between dPS and PnPMA in dPS−PnPMA−L increases and becomes a maximum, and finally decreases, as temperature increases. However, at higher temperatures, miscibility between dPS and PnPMA in dPS−PnPMA−L decreases, becomes a minimum, and finally increases with increasing temperature.

To obtain χ quantitatively, we analyzed the peak corresponding to a correlation hole in the disordered state observed in SANS profiles as follows.[44]

$$\frac{d\Sigma\,(q)}{d\Omega} = v_{\mathrm{ref}}\left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 S(q) \qquad (3)$$

where $d\Sigma(q)/d\Omega$ is the absolute SANS scattered intensity (cm^{-1}), v_{ref} is the reference volume defined as eq 2b, b_i is the neutron coherent scattering length, v_i is the monomeric volume for component i, and $S(q)$ is the structure factor. According to the incompressible RPA due to Leibler,[6] $S(q)$ of a diblock copolymer melt is given by

$$S(q)^{-1} = \frac{F(x,f)}{N} - 2\chi \qquad (4)$$

where $x = R_g^{\,2}q^2$, N is the total number of segments defined as eq 1, f is the volume fraction of dPS, R_g is the radius of gyration of block copolymer, and $F(x,f)$ can be obtained from RPA.[6]

We were well aware that eq 4 is obtained from an assumption of incompressible RPA, but the dPS−PnPMA block copolymer is compressible. Nevertheless, we tried to extract at a given temperature from matching SANS profiles to predictions, since a more elaborate theory including compressibility is not available now.

Figure 7a gives the predictions of SANS profiles by adjusting χ at each temperature. We observed that, even though an incompressible RPA is used, the SANS profiles are well fitted by the prediction of eqs 3 and 4. Furthermore, we did not consider the fluctuation effect of Fredrickson and Helfand,[45] but the qualitative nature of χ depending upon temperature does not change. The temperature dependence of R_g and x^* for dPS−PnPMA−L and dPS−PnPMA−BH in the homogeneous state is shown in Figure 7b. Notice that x^* at each temperature was obtained from the best fit to SANS profiles by using the Leibler theory (eqs 3 and 4). It is seen that the value of x^* was 3.89, which is close to predicted value by the Leibler theory (3.7852) and independent of temperature. On the other hand, R_g was calculated from $(x^*)^{1/2}/q_{\max}$. Since x^* does not change much with temperature, R_g is inversely proportional to $q_{\max}$. Even though dPS−PnPMA−L exhibited a disordered state over the entire temperature range, $q_{\max}$ decreases with increasing temperature at lower temperature region (T < 160 °C). Since the volume (V) of the block copolymer is proportional to R_g ($V \sim R_g^{\,3}$) in the homogeneous state, V increased with temperature at this temperature region. Interestingly, near the LDOT (~170 °C) of dPS−PnPMA−BH, R_g of dPS−PnPMA−L slightly increased. This indicates that the volume change (ΔV) upon LDOT

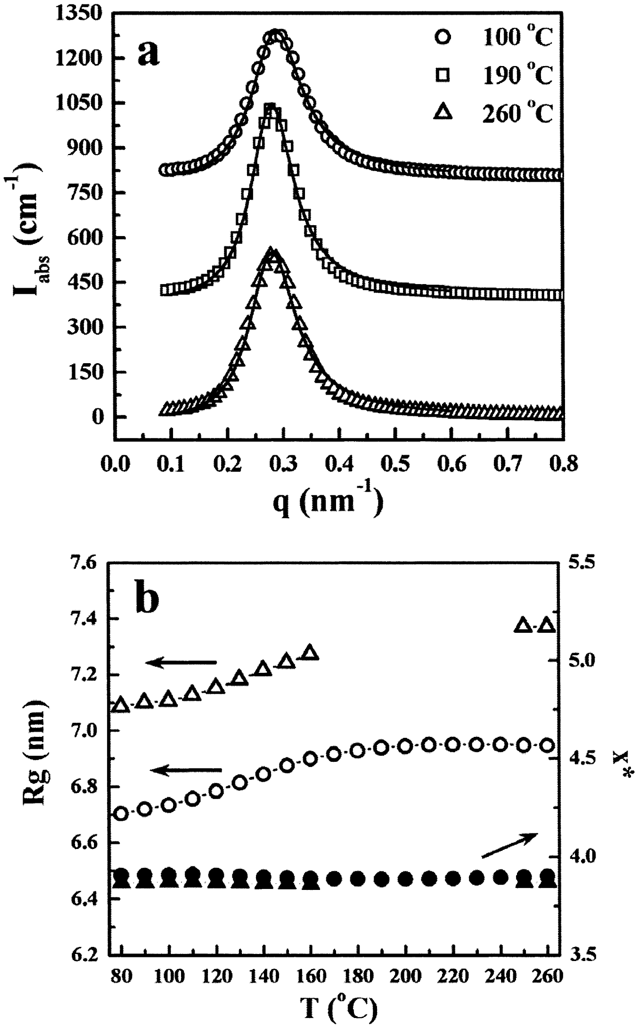

Figure 7. (a) Experimentally measured SANS profiles (symbols) and the predictions (solid curves) by the Leibler mean-field theory (eqs 3 and 4 with eq 2b) for dPS−PnPMA−L at three representative temperatures (100, 190, and 260 °C). (b) Temperature dependence of R_g (open symbols) and x^* (closed symbols) for dPS−PnPMA−L (circle) and dPS−PnPMA−BH (triangle) in the homogeneous state.

might become positive. On the other hand, near the UODT (~250 °C) of dPS−PnPMA−BH, R_g of dPS−PnPMA−L slightly decreased. Thus, ΔV upon UODT might become negative. The different signs for $\Delta V/V$ at two transitions are consistent with experiment results that $\Delta V/V$ measured by dilatometry for dPS−PnPMA−BH becomes positive (~0.2%) at LDOT but negative (~−0.15%) at UODT.[35]

Figure 8a gives the temperature dependence of χ between dPS and PnPMA obtained from dPS−PnPMA−L and dPS−PnPMA−BH in the homogeneous state. Interestingly, with increasing T, χ exhibits two extremes: one is a minimum at a lower temperature, and the other is a maximum at a higher temperature. To the best of our knowledge, this kind of abnormal temperature dependence of χ has not been reported for binary blend and block copolymers. A maximum in χ at high temperature implies a closed-loop type (LDOT and UODT) of phase behavior if N is slightly large. These situations correspond to dPS−PnPMA−BL, dPS−PnPMA−BM, and dPS−PnPMA−BH, as shown in Figure 2a. However, because we clearly see a minimum χ (or χN) in lower temperature for dPS−PnPMA−BH as well as dPS−PnPMA−L, as shown in Figure 8b, dPS−PnPMA has another transition, the so-called "order-to-disorder transition (ODT)" at a lower temperature. This ODT was first suggested in our previous paper,[28] which is reproduced in Figure 9.

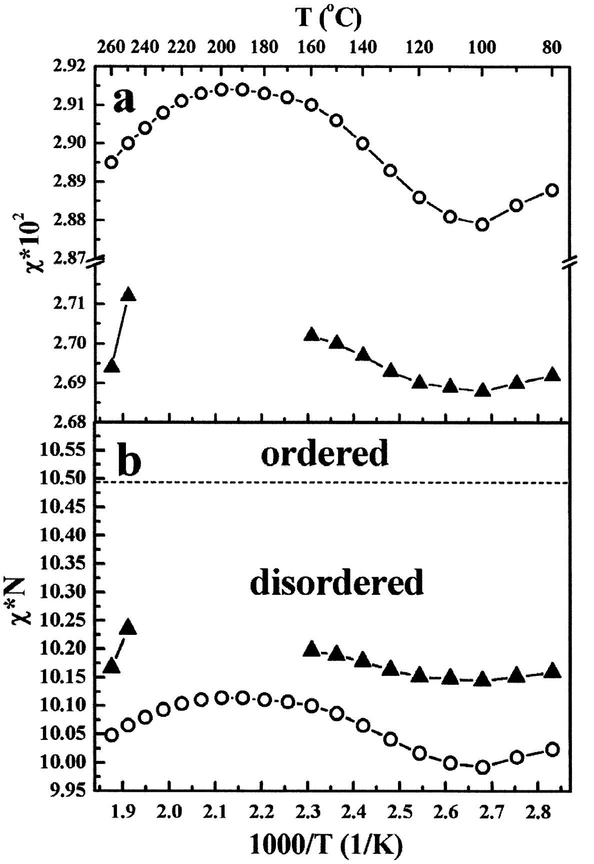

Figure 8. Plots of (a) χ of dPS and PnPMA segments and (b) (χN) vs $1/T$ for two dPS−PnPMAs: dPS−PnPMA-L (○) and dPS−PnPMA-BH (▲). Notice that χ for dSP−PnPMA−BH at temperatures between 180 and 240 °C could not be calculated from SANS profiles on the basis of the Leibler mean-field theory because of ordered phases at those temperatures.

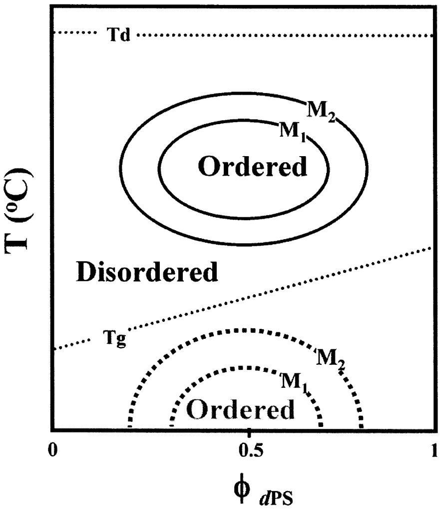

Figure 9. Schematic of phase behavior for dPS−PnPMA with two different molecular weights ($M_2 > M_1$). T_g and T_d are the glass transition and degradation temperatures, respectively.

However, we could not measure this ODT experimentally even though the molecular weight was increased (for instance, dPS−PnPMA−BH). As seen in Figure 8b, the value of χN of dPS−PnPMA−BH is still less than 10.495 even at a temperature as low as ~80 °C, which is the lowest experimental temperature due to the T_g (~57 °C) of homogeneous block copolymer.[46] In order for ODT to be seen, M_n in a dPS−PnPMA should be larger than that of dPS−PnPMA−BH. One possible choice is dPS−PnPMA−H. However, this block copolymer exhibited LAM microdomains over the entire temperature range. Because T_g of dPS block in dPS−PnPMA−H was determined to be ~100 °C, SANS profiles measured experimentally at lower temperatures than 100 °C do not correspond to equilibrium morphology; rather, those would be reflected from kinetically frozen nonequilibrium morphology. Thus, we could not detect the ODT experimentally for dPS−PnPMA even if it indeed existed.

On the other hand, we reported that dPS/PnPMA blend has both UCST and LCST at lower and higher temperatures.[32] We are confident that PS−PnPMA (or dPS−PnPMA) has an ODT which is shown as dotted curves in Figure 9. Exactly why PS−PnPMA (or dPS−PnPMA) has the complex phase behavior given in Figure 9 is not clear. But, qualitatively, we explain this peculiar behavior considering three temperature regimes: (a) Lower temperatures: Here, enthalpy (positive contribution to free energy) dominates the combinatorial entropy. Also, the free volume term is negligible. Thus, an ODT is expected since enthalpy steadily decreases with increasing temperature. (b) Intermediate temperatures: The free volume term prevails over combinatorial entropy, which induces the LDOT. (c) Higher temperatures: Here, translational entropy again prevails over the free volume, which results in the UODT.

We found that asymmetric dPS−PnPMA (or PS−PnPMA) with hexagonally packed cylinder or body-centered-cubic microdomains have two transitions of LDOT and UODT consisting of a closed loop, which were determined by SAXS, rheology, and TEM.[48] Thus, a closed loop given in Figure 9 indeed represents the phase behavior dPS−PnPMA (or PS−PnPMA), although the exact boundary between ordered states in a closed-loop phase diagram is currently under investigation.

Before closing, a question might be raised why an upper UCST was not observed for dPS/PnPMA (or PS/PnPMA) blend. If the phase behavior of the dPS/PnPMA blend were to be similar to that of dPS−PnPMA copolymer, a maximum in χ should have appeared at higher temperatures. However, as we reported previously,[32] we could not find a maximum in χ up to the degradation temperature (~270 °C) of PnPMA. Thus, it may be possible that a maximum in χ should be observed at very high temperatures once polymer does not degrade, which suggests the existence of an upper UCST. It is noted that the theoretical model in refs 23 and 24 indeed predicts an upper UCST for dPS/PnPMA blend at 5130 K, which is much higher than the degradation temperature.[32]

On the other hand, there is another aspect pointed out by Dudowicz and Freed.[16] Namely, the $1/N$ contribution to χ for block copolymer arising from the connectivity becomes very important compared with the corresponding polymer blend; thus, the upper UCST would not be observed in principle for dSP/PnPMA blends even at a very high temperature where PnPMA is assumed not to degrade. Or, as pointed out by Bates and co-workers,[49] χ obtained from the mean-field theory using a block copolymer in the homogeneous state might not be the same as that obtained from homogeneous polymer blends. This subject should be clarified later.

IV. Conclusions

In this study, we have shown, via SAXS, SANS, and rheology, that dPS−PnPMA exhibited a closed-loop phase behavior, as did hPS−PnPMA. As the molecular weight (or N) of dPS−PnPMA decreases, the size of the loop decreases and the closed-loop finally vanishes when N is smaller than a critical value. We found for the first time an abnormal temperature dependence of χ between dPS and PnPMA segments; namely, with increasing T, χ exhibits two extremes: one is a minimum at a lower temperature, and the other is a maximum at a higher temperature. A maximum in χ at high temperature implies a closed-loop type (LDOT and UODT) of phase behavior. But, because of the existence of a minimum χ, this block copolymer gives another transition of ODT at a lower temperature. This ODT is related to UCST found for the dPS/PnPMA blend.

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